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On the Research of adsorption of Polycyclic Aromatic Hydrocarbons (Phenanthrene) in Soil-Groundwater in Zhangshi Irrigation District

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Abstract

The thesis mainly studies the dynamic variation features of absorption of polycyclic aromatic hydrocarbons (PAHs) in soil and groundwater of Zhangshi irrigation district in southwest part of Shengyang City of China. On the basis of the field inspection on hydrogeochemistry of Zhangshi irrigation district, we choose four typical sites, taking samples from surface soil layer, sub-vadose zone and acquifer to do experiment of dynamic successive absorption on phenanthrene as the typical pollutant. And we also study the absorptional dynamics characteristics of phenanthrene in soil and groundwater. Linear models and Freundlich models are also used to simulate the absorption isotherm. The results show two outstanding phases of phenanthrene adsorption in underground environment: the quick linear partition phase and the slow nonlinear adsorption phase. Phenanthrene adsorption is in positive correlation with the organic contents in soil. Whereas the balance time of adsorption is in negative correlation with the organic contents in soil. Since the adsorption curve is a typical "S" type in the organic-rich top soil, the tendency shows the likeliness of multilayer adsorption. The partition function of solid phase and liquid phase of phenanthrene in the relatively poor organic lower vadose zone shows certain linear relationship. The adsorption of phenanthrine in organic-poor acquifer soil particles belongs to linear adsorption. The relevant factors R are all above 0.9627.

Keywords: PAHs; Phenanthrene; Soil; Groundwater; Vadose zone; Acquifer; Adsorption; POPs

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of toxic xenobiotic fused-ring aromatic compounds consisting of hydrocarbon molecules of two or more fused benzene and/or pent acyclic rings in linear, angular or cluster formation (Jiao et al, 2007; Baumard et al, 1998;). They are widespread environmental pollutants (Fromme et al, 2004; Tao et al, 2006; su et al, 2008), with particularly the higher molecular weight compounds representing a

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serious threat to human health due to their mutagenic and carcinogenic properties (Kipopoulou and Samara, 1999; Kurunthachalam et al, 2008). However, very little is known about the long term effects these compounds have on soil micro biota. The absorption study of PAHs in soil and sediment is significant to the understanding pollutants transfer fate. It has also become the hot spot in the current research.

Soil is the important environment medium for PAHs accumulation and transfer (Zhu et al, 2009; Liu et al, 2006; Ni et al, 2008). PAHs in absorption are influenced by rainwater infiltration and sewage irrigation, which might cause desorption to release PAHs into the environment (Ruchaya et al. 2006; Yim et al, 2007; Christensen et al, 1997). Then it is transferred to aquifer through aeration zone of soil, which causes pollution of groundwater. Thus difficulties and costs of repairing are greatly enlarged (Lai et al, 2009; Zhu et al,2004). Therefore the study of absorption of typical pollutants like phenanthrine in vertical profile media of topsoil, lower aeration zone and aquifer plays an important role in controlling and repairing soil-groundwater system that is polluted by PAHs.

This study mainly samples soil of topsoil, lower aeration zone and aquifer in vertical profile of the four point positions of typical environment function area. Serial continuous absoption-desorption experiment is carried out to inspect phenanthrine absorption in aeration zone and aquifer. It provides a theoretical foundation for the prediction of PAHs transfer and transformation rule in soil-groundwater environment and pollution prevention of organic pollutants in soil.

2. Materials and Methods

2.1. Soil Sample

Soil sample for experiment is taken from Zhangshi irrigation district in southwest part of Shengyang City. Sampling sites (S1, S2, S3 and S4) are located respectively in the north bank of Hunhe River to the south of Zhangshi irrigation district, west of Yangshitun, east of Zhangyizhen and south of Xihe River. The depth is 1.5-2.2 m. We remove soil debris such as rock, plant branches and leaves and etc. Then the soil is air dried, mashed and sifted for later use. According to the condition of site hydrogeological investigation and shallow groundwater depth, in combined consideration of differences concerning texture characteristics of soil profile in topsoil, lower aeration and aquifer, also taking research facility into consideration, we divide classify each soil profile in unity into upper, middle and lower layers, which are namely topsoil (layer A), lower aeration zone (B layer) and aquifer (C layer). The physical and chemical parameters of samples are shown in Table 1.

Tabel 1. The mechanical composition and the main properties of soil samples

Position	Code	Layer	Depths /cm	pH	f_{oc} /(g • kg-1)	Sample Texture
	S1-A	Top Soil	0～30	7.38	18.21	Sandy Soil
S1	S1-B	aeration zone	30～150	7.23	13.33	Clay
	S1-C	aquifer	150～250	6.77	9.25	Light Sandy Soil
	S2-A	Top Soil	0～30	7.15	23.32	Clay
S2	S2-B	aeration zone	30～150	7.02	40.38	Clay
	S2-C	aquifer	150～250	6.98	17.61	Light Sandy Soil
	S3-A	Top Soil	0～30	7.35	27.6	Loamy Clay
S3	S3-B	aeration zone	30～150	6.25	13.91	Clay
	S3-C	aquifer	150～250	6.37	11.66	Sandy Soil
	S4-A	Top Soil	0～30	6.95	20.65	Triturated Clay
S4	S4-B	aeration zone	30～150	7.52	15.23	Sandy Clay
	S4-C	aquifer	150～250	7.12	10.12	Sandy Soil

2.2. Main Reagent Equipment

Phenanthrine made by German Fluka Company, color spectrum pure; potassium nitrate, analysis pure; American Afilent6890GC/5973MSD; WR11-HZ100 shaker; type LDZ5-2 electrical centrifuge; BS224S electric balance.

2.3. Sample Preparation and Analysis

Preparation of phenanthrine saturated water solution: Measure some phenanthrine reagent (color spectrum pure). Solve it in some methanol to prepare methanol solution of phenanthrine with relatively high concentration. Then dilute it with water to make oversaturated solution of phenanthrine (volume ratio of methanol and water should be 3% maximum). When in use, dilute it into phenanthrine water solution with different concentration.

Extract in the way of accelerated solvent extraction (DIONEX ASE2300). Then purify by means of column chromatography. The chromatographically separated sample should then be remained at constant volume of 1ml with hexane after it goes through rotary evaporation. Cold storage is needed. Refer to Tao's methods with testing repetition rate of 50% (Tao et al, 2004). The detection limit should be 0.06 μg/kg.

2.4. Desorption Test

Weigh respectively 3.5 g of undisturbed soil from different depths in S1, S2, S3 and S4. Put them into 250 ml conical flask with cover. Pour the prepared 210 ml saturated solution of phenanthrine and tighten the cover. Seal it with tinfoil. Shake at 200 r/min in type CHZ82 Guohua digital constant temperature oscillator. Take 20 ml balanced solution at 20 min, 40 min, 60 min, 90 min, 120 min, 240 min and 480 min from each layer samples (The pre-experiment shows 8 hour is enough to reach adsorption equilibrium). Centrifuge it at 3000 r/min for 15 min with centrifuge machine. Take supernatant and measure phenanthrine concentration in it. After the experiment, draw the variation curves of phenanthrine concentration varied with time in solution and phenanthrine absorption volume change with time.

3. Result and Discussion

3.1. Phenanthrine Absorption Dynamics Characteristics

Figure1 shows that phenanthrine reaches balance of absorption in 24 hour. Because the solid phase concentration no longer changes after 24 hour, 24 hour absorption volume can be regarded as the balance absorption capacity. About 40 min after the beginning of the test, phenanthrine concentration of the four point samples is rapidly increased. 90 min after the test, phenanthrine absorption volume can reach 85% of the total quantity of saturated absorption. Around 2 hour later, 98% is reached. In about 5 hour, 99% is basically reached. So 8 hour can be taken as the absorption equilibrium time.

The result of absorption dynamic test shows that the absorption of phenanthrine in the four point samples of each layer undergoes two obvious stages: fast linear distribution stage and slow nonlinear absorption stage. In the beginning of the test, phenanthrine is rapidly absorbed in the surface of soil particle, with the slowing down of absorption rate, the process reaches absorption balance. However, time for each point and each layer sample to reach absorption balance is different. It increases with sampling depths generally. With the phenanthrine absorption capacity lowered, time for absorption balance is gradually reduced, which shows the close relations between phenanthrine absorption and soil sample physical and chemical characteristics. For example, at the start, the samples of the three layers on S1 point position absorb phenanthrine increasingly fast. Yet variation exists for the increase rate in each layer. Within 20 min, SI-A, S1-B and S1-C reach above 60%, 65% and 70% of balance absorption capacity respectively. At 20-90 min, absorption capacity of phenanthrine of each layer decreases, among which S1-C decreases fastest, and S1-B being the next. In 2 hour absorption stabilizes gradually with absorption of each layer of samples reaching 98%. Absorption is almost balanced.

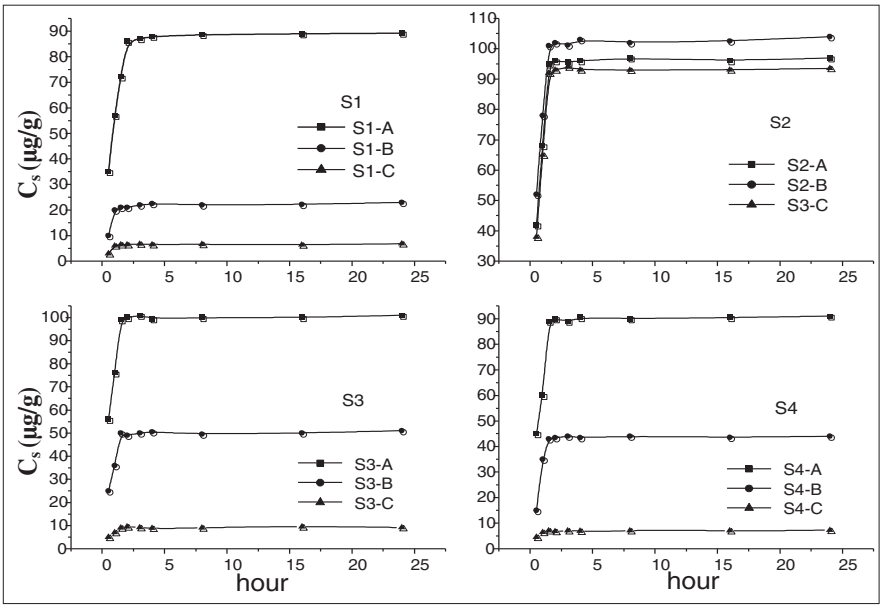

Fig. 1. Schematic Diagram of Physical Model of Phenanthrene Environmental Fate in Soil-Groundwater System

Phenanthrine absorption speed and its capacity are mainly decided by the available absorption points in soil and organic substances. Firstly, phenanthrine absorption capacity is in positive correlation with organic content in soil. Because organic content in aeration zone is higher than that in aquifer, when absorption reaches balance, phenanthrine absorption capacity of each soil sample layer is identical both in size and order to their organic content which is basically A>B>C; but phenanthrine absorption of each layer of S2 being B>A>C., which agrees with its organic content . Secondly, absorption balance time of each layer is in negative correlation with soil organic content. It is because of the two different processes of phenanthrine absorption in soil, fast process and slow process. The initial fast process shows that phenanthrine reaches hydrophobic surface rapidly and transfers to soil matrix difficult to get to. That slow process can last very long time. It does not stop until the absorption capacity of soil organic is depleted and balanced. It is particularly showed by the absorption capacity increases fast when phenanthrine is absorbed to the surface of soil particle at the beginning stage of absorption. With time passing by, hydrophobic points in soil easy to absorb are occupied. Phenanthrine begins to disperse into interior soil particle near hydrophobic points inside soil difficult to absorb. Then absorption speed is lowered to reach the ultimate absorption balance. Therefore in soil containing relatively less organic substance, organic ability is rapidly depleted during the period when control steps are reduced.

3.2. Isotherm of Phenanthrine Absorption

Isotherm of phenanthrine absorption in each layer of soil of the four points is shown in Figure 2 which shows absorption capacity increases with liquid phase concentration by the general curve tendency. In organic rich soil (S1-A, S2-A, S2-B, S3-A, S4-A, S4-B), when the liquid phase concentration is lower than 100 μg, absorption capacity increases steadily by linear increase trend. When the concentration is higher than 100 μg, absorption capacity increases promptly by leaping. Then it flattens. The entire curve shows ladders. This type of curve is a typical “S” shape absorption curve. The tendency might show multi-molecular layer absorption. While in organic relatively poor soil (S1-B, S1-C, S2-C, S3-B, S3-C, S4-C), phenanthrine serves mainly distribution function

between solid phase and liquid phase, which shows a certain linear relationship. From Figure 2 we can also observe the linear absorption of phenanthrine in the soil.

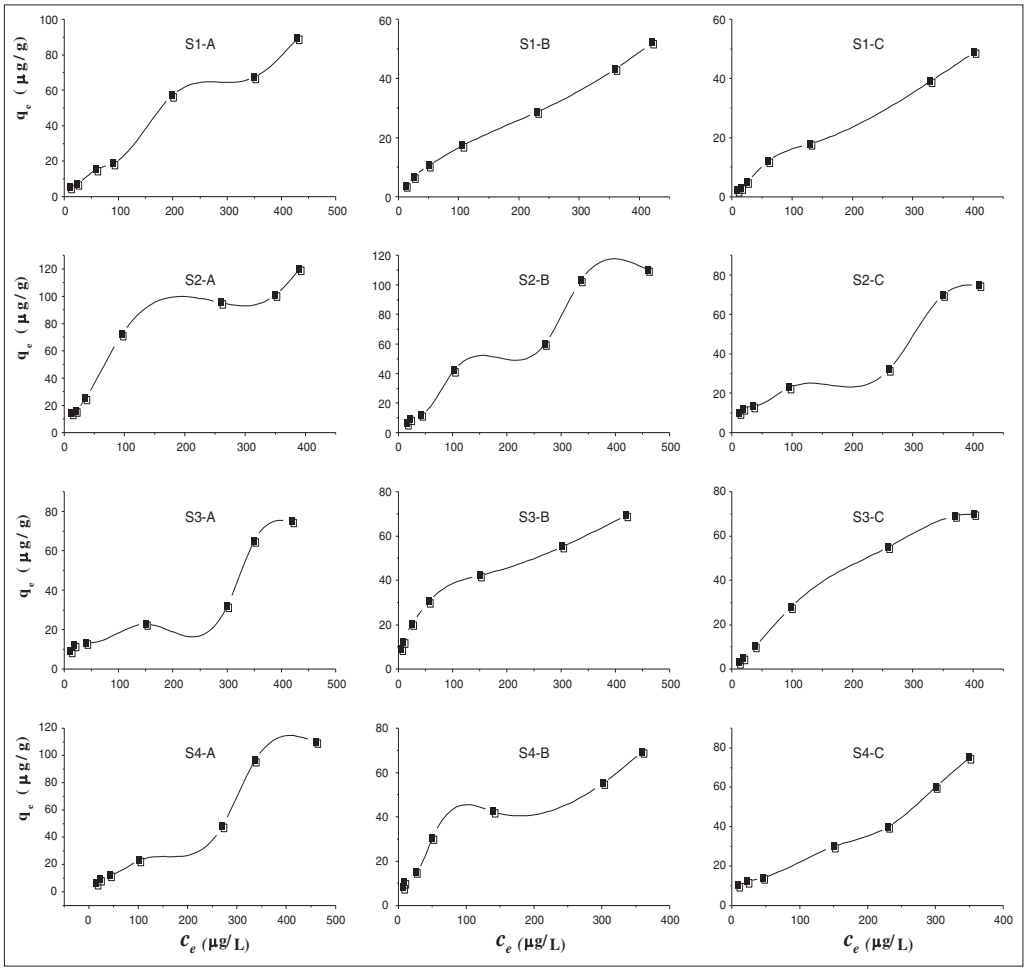

Fig. 2. Isotherms for adsorption of phenanthrine

3.3. Parameters of Isotherm of Phenanthrine Absorption

In phenanthrine solution, solute absorption of soil is a dynamic process. At fixed temperature, when absorption is balanced, absorption isotherm can show the relationship between soil surface absorption q_e and balance concentration of phenanthrine in solution. C_e Absorption isotherm is usually described by the following formula:

Linear model:

$$q_e = K_D C_e \tag{1}$$

Freundlich absorption model：

$$q_e = K_F C_e^n \tag{2}$$

Or its logarithmic equation：

$$\log q_e = n \log C_e^n + \log K_F \tag{3}$$

In the above, K_D is balance absorption constant of absorption substance, K_F is a constant under Freundlich model related with absorption capacity and absorption strength. n is used to show nonlinear size of absorption isotherm. When $n=1$, it shows linear distributive isotherm; when $n<1$ nonlinear isotherm is showed.

Phenanthrine isotherm of soil in aeration zone and aquifer of the four points is actually mapped. Meanwhile phenanthrine absorption isotherm is simulated with linear model and Freundlich model. The results listed in Table 2 show the following characteristics:

- The linear model well simulates the absorption testing data of S1-B, S1-C, S2-C, S3-B, S3-C, S4-C. S1-B and S3-B are soil sample of aeration zone. S1-C, S2-C, S3-C and S4-C are all soil samples of aquifer. This shows that phenanthrine absorption on soil particle poor in organic in aquifer belongs to linear absorption. The relevant coefficients R are all higher than 0.9627.
- Freundlich model well simulates the absorption data of S1-A, S2-A, S2-B, S3-A, S4-A, and S4-B. All samples are aeration zone soil rich in organic. Their values are between 0.5637～0.8784. This shows the obvious display of nonlinear phenanthrine absorption process. The relevant coefficients R are all higher than 0.9759. When concentration high, there is a big deviation between testing value and calculation value, which derives from the limitation of application of Freundlich model, i.e., limitation of low concentration.

Table 2. Phenanthrine soil samples in the four places on the adsorption isotherm coefficient

Sample Code	Linear Model		Freundlich Model		
	K_D	R	$\log K_F$	n	R
S1-A	**0.2119**	**0.9822**	**-0.3650**	**0.8784**	**0.9893**
S1-B	**0.1245**	**0.9979**	**-0.1969**	**0.7158**	**0.9974**
S1-C	**0.1227**	**0.9970**	**-0.4610**	**0.8237**	**0.9967**
S2-A	**0.2592**	**0.9742**	**-0.290**	**0.6429**	**0.9759**
S2-B	**0.3257**	**0.9533**	**-0.2286**	**0.8617**	**0.9832**
S2-C	**0.1802**	**0.9627**	**0.2453**	**0.5907**	**0.9527**
S3-A	**0.1646**	**0.9428**	**-0.2650**	**0.5637**	**0.9848**
S3-B	**0.1851**	**0.9698**	**0.6763**	**0.4400**	**0.9962**
S3-C	**0.1887**	**0.9894**	**-0.3594**	**0.8633**	**0.9946**
S4-A	**0.2409**	**0.9756**	**-0.3016**	**0.8466**	**0.9809**
S4-B	**0.2032**	**0.9653**	**-0.5303**	**0.5670**	**0.9864**
S4-C	**0.2026**	**0.9857**	**0.1049**	**0.6619**	**0.9753**

With regards to aeration zone soil S1-A, S2-A, S2-B, S3-A, S4-A and S4-B as shown by Figure 2, when the liquid phase concentration is lower than 100 μg, absorption capacity increases steadily by linear increase trend. When the concentration is higher than 100 μg, absorption capacity increases promptly showing nonlinear characteristic. Both linear model and Freundlich model reflect distribution heterogeneity and nature difference of soil organic substances. Due to the differences of organic substances of soil, when the concentration of organic pollutants is low, the absorption pattern is mainly surface absorption. Pollutants are absorbed firstly on the organic substances with powerful absorption ability, which shows noticeable linear character in absorption process. When the concentration of organic pollutants is high, absorption patterns point absorption chiefly. The number of organic substances in soil is the main influential factor, which shows a certain nonlinear feature. That may be the reasons for this phenomenon.

K_F is a relevant constant to absorption capacity and absorption strength under Freundlich model. Table 2 shows that the size order of it is S2-B>S3-A>S2-A>S4-A>S1-A>S4-B. Moreover, the organic carbon content order in samples as shown in Table 1 is S2-B>S3-A>S2-A>S4-A>S1-A>S4-B. The two orders are identical. Both show linear relationship, which means that organic substances are the main components. With the reduction of organic substance in samples, the absorption to phenanthrine is reduced. Figure 3 shows the linear relationship between the

coefficient K_F representing sample absorption capacity and that of f_{oc} representing organic carbon contents. Figure 3 shows its fitting linear regression equation.

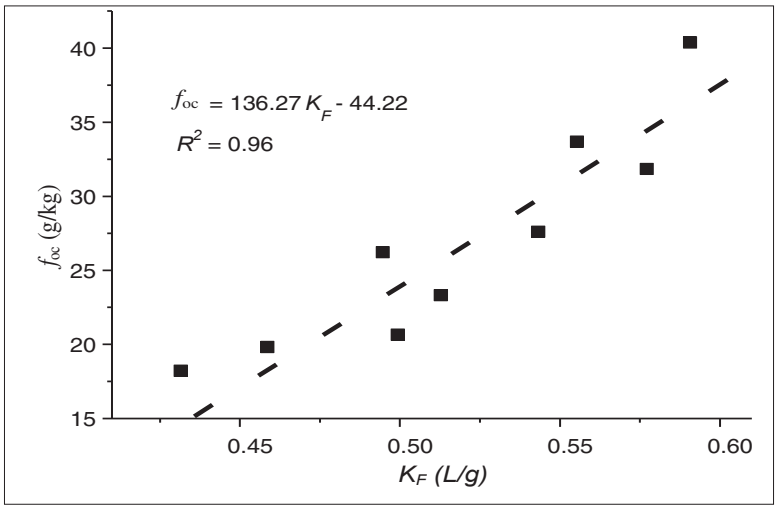

Fig. 3. Relation between K_F and f_{oc}

4. Conclusion

From the above account we can draw the following conclusion by the study on the phenanthrine absorption and desorption experiment in groundwater environment.

- 90 min after the test, phenanthrine absorption volume can reach 90% of the total quantity of saturated absorption. Around 2 hour later, 98% is reached. In about 5 hour, 99% is basically reached. So 8 hour can be taken as the absorption equilibrium time. It is within 30min that phenanthrine desorption reaches 85% of the total volume. In about 1h, more than 95% is reached. 98% is reached in 4 hour. We take 8 hour as desorption balance time to ensure the reliability of the test. Phenanthrine concentration desorbed out of soil almost remains the same in 1.5 hour, approaching unity. After phenanthrine is absorbed by soil, it can be desorbed. But desorption capacity is relatively low. Phenanthrine desorption degree in each layer of soil is smaller than 10%.
- The absorption of phenanthrine in underground environment undergoes two obvious stages: fast linear distribution stage and slow nonlinear absorption stage. Generally speaking, with the increase of sampling depths, phenanthrine absorption capacity of phenanthrine in aeration zone and aquifer is decreased gradually. Time for absorption to reach balance is also different, being basically shortened gradually. It shows the close relationship between phenanthrine absorption behavior and the physical and chemical characteristics of soil samples.
- Phenanthrene adsorption is in positive correlation with the organic contents in soil. Phenanthrine absorption capacity of phenanthrine in each layer of soil sample is the same as its organic contents in order, ehich is basically A>B>C. And the balance time of adsorption is in negative correlation with the organic contents in soil.
- The organic constituents and inorganic constituents in aeration zone and aquifer are different. Thus the absorption patterns and absorption mechanism are varied too. In organic-rich soil, when the liquid phase concentration is lower than 100 μg, absorption capacity increases steadily by linear increase trend. When the concentration is higher than 100 μg, absorption capacity increases promptly by leaping. Then it flattens. The entire curve shows ladders. This type of curve is a typical “S” shape absorption curve. The tendency might show multi-molecular layer absorption. While in organic relatively poor soil, phenanthrine serves mainly distribution

function between solid phase and liquid phase, which shows a certain linear relationship. Phenanthrine absorption on soil particle which is poor in organic in aquifer belongs to linear absorption. The relevant coefficients R are all higher than 0.9627. Freundlich model well simulates aeration zone soil that is rich in organic. Their values are between 0.5637～0.8784. This shows the obvious display of nonlinear phenanthrine absorption process. The relevant coefficients R are all higher than 0.9759.

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